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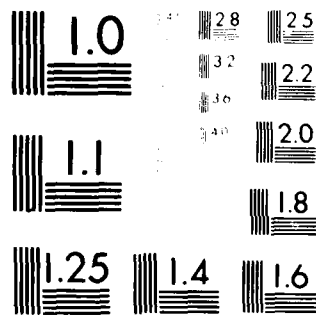   MAY 80   D J WHELAN
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TECHNICAL NOTE

MRL-TN-437

THE DENSITY OF SEAWATER : SOME PRACTICAL RELATIONSHIPS

Daniel J. Whelan

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DEPARTMENT OF DEFENCE

MATERIALS RESEARCH LABORATORIES

TECHNICAL NOTE

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THE DENSITY OF SEAWATER : SOME PRACTICAL RELATIONSHIPS

Daniel J. Whelan

ABSTRACT

Traditionally, the density of seawater as a function of temperature and salinity at atmospheric pressure has been discussed in terms of the density function, Sigma-T, and, in this report, some simplified mathematical relationships are presented from which changes in Sigma-T can be predicted from changes in temperature and salinity.

However, density is also affected by pressure and an accurate treatment of the density of seawater within a deep ocean water mass requires a more sophisticated approach. An outline of one such treatment and the results obtained from it are given in detail.

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DOCUMENT CONTROL DATA SHEET

1. **DOCUMENT NUMBERS:**

   a. AR Number: AR-002-158

   b. Series & Number: TECH.NOTE MRL-TN-437 ✓

   c. Report Number: MRL-TN-437

2. **SECURITY CLASSIFICATION:**

   a. Complete document: UNCLASSIFIED

   b. Title in isolation: UNCLASSIFIED

   c. Abstract in isolation: UNCLASSIFIED

3. **TITLE:**

   THE DENSITY OF SEAWATER : SOME PRACTICAL RELATIONSHIPS

4. **PERSONAL AUTHOR(S):**

   WHELAN, Daniel J.

5. **DOCUMENT DATE:** MAY, 1980

6. **TYPE OF REPORT & PERIOD COVERED:**

7. **CORPORATE AUTHOR(S):**

   Materials Research Laboratories ✓

8. **REFERENCE NUMBERS:**

   a. Task: Marine Chemistry 78/150

   b. Sponsoring Agency: Defence

9. **COST CODE:** 284420

10. **IMPRINT (Publishing establishment)**

    Materials Research Laboratories,
    P.O. Box 50, Ascot Vale, Vic.3032

    MAY, 1980

11. **COMPUTER PROGRAMME(S):**
    (Title(s) and language(s)):

12. **RELEASE LIMITATIONS (of the document):**

    Approved for Public Release

12-0. **OVERSEAS:** | N.O. | | P.R. | 1 | A | | B | | C | | D | | E | |

13. **ANNOUNCEMENT LIMITATIONS (of the information on this page):**

    No Limitation

14. **DESCRIPTORS:**

    630   Sea water   Density (mass/volume)
    645   Specific volume

15. **COSATI CODES:** 810   1407

16. **ABSTRACT** (if this is security classified, the announcement of this report will be similarly classified):

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C O N T E N T S

*   *   *

THE DENSITY OF SEAWATER : SOME PRACTICAL RELATIONSHIPS

1. INTRODUCTION

Over the past five years, the Marine Environment Group of the Materials Research Laboratories has conducted a series of oceanographic cruises in order to characterise the physical and chemical environment of the ocean waters around Australia, some of which may have specific long-term operational significance. Reports summarising results from four such cruises have recently been published [1-4].

During each cruise, several stations were occupied and, at each station, water samples were taken and subsequently analysed for variations with depth of temperature, salinity, pH and alkalinity, dissolved oxygen, etc. From the data thus accumulated, various calculations can be made on the expected dynamic properties of the ocean mass, including profiles of the velocity of sound [5], its absorption and transmission in seawater [6,7], water transport and circulation [8,9] and the stratification of waters within the ocean [9].

With regard to this last-mentioned property, it has become apparent, from the author's discussions, that even some experienced oceanographers blithely discuss variations in the density of seawater with depth entirely in terms of the well-known density function, "Sigma-T", σ_T. It appears that they do not appreciate that Sigma-T is strictly a surface property, calculated for water at atmospheric pressure, and that the time-honoured tables and formulae relating changes in salinity, S, and temperature, T, with changes in density [10,11] refer to properties at 1 atm pressure, only.

In their classic text, Sverdrup, Johnson and Fleming [12] pointed out that the density of water is a function not only of temperature and salinity but also of pressure, and that changes in density with depth do occur and cannot be neglected, especially when deep ocean water masses are being considered. This point is taken further by Mamayev [13] and, in a different context, by Chen and Millero [14], inter alia. It is the purpose of this report to reaffirm the true situation and to show how the density function is affected by changes in temperature, salinity and pressure.

2. DENSITY, SPECIFIC GRAVITY AND SPECIFIC VOLUME (Ref 13)

Density and specific volume are complementary terms. The density of water, ρ, represents the mass contained in a unit of volume, while the specific volume, V, represents the volume of liquid occupied by a unit mass. The two are related, thus

$$V\rho = 1 \tag{1}$$

Both of these parameters are functions of temperature, T, pressure, P, and salinity, S, so that, more correctly, they should be written

$$\rho = \rho(S,T,P) \tag{2}$$

and
$$V = V(S,T,P) \tag{3}$$

In establishing the interrelation between these variables, one endeavours to arrive at a practical equation of state of seawater.

Oceanographers have adopted an approach of defining the specific gravity of seawater, $s_T = s_T(T,S)$, at atmospheric pressure, so that

$$s_T = \frac{\text{density of seawater at } T^\circ C}{\text{density of pure water at } 4^\circ C} \tag{4}$$

and, in order to accentuate the relative magnitude of changes in density between different samples of water, they have introduced a new term, Sigma-T, σ_T, defined by the equation

$$\sigma_T = (s_T - 1) \times 10^3 \tag{5}$$

an idea apparently going back to the time of Knudsen, or earlier [15].

In order to relate changes in temperature and salinity to changes in density or Sigma-T, great care has been taken to measure density and evaluate Sigma-T for selected seawater samples [11] and these measurements have become the basis for the various hydrological tables and relationships currently in use [10,11].

In our work, we are making considerable use of the relationship determined by Cox, McCartney and Culkin [11]. This relationship was derived from results from some fifty surface water samples taken from several different northern hemisphere oceans. The measured values of Sigma-T were fitted mathematically to an equation of the following form,

2

$$\sigma_T = \sum_i \sum_j a_{ij} T^i S^j \ ,$$

$$3 \geqslant (i \text{ and } j) \geqslant 0 \ , \tag{6}$$

for $41 \geqslant S \geqslant 9$ parts per thousand (ppt)

and $25 \geqslant T \geqslant 0$ °C.

The values of the coefficients a_{ij} in this equation are given in Table 1.

Although this equation gives an accurate description of σ_T, it may be considered somewhat unwieldy for those enthusiasts wishing to carry out on-the-spot calculations, while reclining on a hammock on board ship [16]. To cater for this situation, the following simplified equation proposed by Mameyev appears to be well suited :

$$\sigma_T \simeq 28.15 - 0.0735T - 0.00469T^2$$

$$+ (0.802 - 0.002T)(S-35) \tag{7}$$

for $36 \geqslant S \geqslant 32$ ppt and $30 \geqslant T \geqslant 0$°C,

and it is from this equation that one can readily estimate how sensitive σ_T is to changes in temperature and salinity under surface conditions.

From eqn.7, one obtains, for $S = 35$ ppt,

$$\frac{\partial \sigma_T}{\partial T} \simeq -0.0735 - 0.0094T \qquad (°C)^{-1} \tag{8}$$

and $$\frac{\partial \sigma_T}{\partial S} \simeq 0.802 - 0.002T \qquad (ppt)^{-1} \tag{9}$$

In Table 2, changes in σ_T for seawater at 25°C and 35 ppt salinity have been calculated from these equations and compared with changes calculated from hydrological tables and from eqn.6.

The apparent justification for calculating Sigma-T values from salinity and temperature values over a vertical water mass is that it assists in defining the various bodies of water in the mass. However, as defined above, Sigma-T depends on salinity and temperature only, referring to an equation of state at 1 atmosphere (100 kPa) pressure, so any comparison of Sigma-T

values obviously refers to properties of that water, at 1 atmosphere pressure, not in situ.

In addressing the problem of the influence of pressure on density of seawater, Defant [17] derived the following simplified formulae for the determination of specific volume and density in situ in a standard ocean mass (35 ppt S, 0°C) at a pressure p decibars (corresponding approximately to a depth z metres, where $|p| = |z|$) or 10p kPa,

$$10^5 \ V(35,0,p) \ = \ 97264 - 0.44p \quad cm^3 g^{-1} \tag{10}$$

and
$$10^5 \ \rho(35,0,p) \ = \ 102813 + 0.46p \quad g \ cm^{-3} \tag{11}$$

Converting eqns. 10 and 11 to SI units, one obtains

$$10^8 \ V(35,0,p) \ = \ 97264 - 0.44p \quad m^3 \ kg^{-1} \tag{10a}$$

and
$$10^2 \ \rho(35,0,p) \ = \ 102813 + 0.46p \quad kg \ m^{-3} \tag{11a}$$

If the density factor $\sigma_T(S,T,P)$ is introduced and defined by the equation

$$\sigma_T(S,T,P) \ = \ (s_T(S,T,P) - 1) \ x \ 10^3 \tag{12}$$

where the specific gravity of seawater in situ is defined as

$$s_T(S,T,P) = \frac{density \ of \ seawater \ in \ situ}{density \ of \ pure \ water \ at \ 4°C, \ 100 \ kPa \ pressure} \tag{13}$$

then, from eqn.11,

$$\sigma_T(35,0,p) \ \simeq \ 28.13 + 0.0046p \tag{14}$$

At a depth of 1000 m, the correction to $\sigma_T(S,T)$ corresponds to ca 4.6, although it should be stressed that eqns.10 and 11 are only approximate and are based on near-surface calculations.

4

3. THE EFFECT OF PRESSURE ON THE DENSITY OF SEAWATER

Defant's relationships, summarised by eqns.10, 11 and 14, are useful in that they impress on the reader that pressure effects on the density of seawater are considerable and cannot be neglected in ocean dynamics. In seawater, hydration of ions, perturbation of chemical equilibria and effects on the structure of water itself are all influenced by changes in pressure and are all potentially amenable to physicochemical studies (for example, Ref. 18-20).

In addition, there has been considerable effort, particularly over the last twenty years, devoted to the formulation of an accurate equation of state, relating the specific volume of seawater to pressure and temperature changes; this can be done either by direct measurement of thermal expansibility, α^P, or isothermal compressibility, β^P, or from the propagation of sound in seawater [21].

Thermal expansibility, α^P, and isothermal compressibility, β^P, are defined by

$$\alpha^P = \frac{1}{V^P} \frac{\partial V^P}{\partial T}$$

and

$$\beta^P = \frac{-1}{V^P} \frac{\partial V^P}{\partial P}$$

where V^P is the specific volume of the medium, here seawater, at an applied pressure, P, and temperature, T.

The present status of this work has recently been reviewed and extended by Chen and Millero [14], using the most accurate, currently available data in the literature.

In brief, Chen and Millero expressed the secant bulk modulus of seawater, K, defined by eqn.15, in terms of a second-degree polynominal in P, eqn.16

$$K = \frac{P \ V^O}{V^O - V^P} \tag{15}$$

$$= K^O + AP + BP^2 \tag{16}$$

where K^O, A and B are salinity- and temperature-dependent parameters and V^O the specific volume at zero reference pressure.

They rearranged these equations for V^P and calculated $\dfrac{\partial V^P}{\partial T}$ and $\dfrac{\partial V^P}{\partial P}$, which are related to the speed of sound in a compressible fluid [21].

The speed of sound in seawater as a function of salinity, temperature and pressure (depth) can be calculated (for example, Ref. 5). From a knowledge of the densities of pure water and seawater at 100 kPa (1 bar) [11,22,23], Chen and Millero used iterative techniques in order to calculate coefficients in a set of expressions defining K^O, A and B and consistent with the known isothermal compressibilities and thermal expansibilities of seawater.

Their equation of state, derived for seawater over a salinity range 0-40 ppt, temperature range 0-40°C and pressure range $0-10^5$ kPa (0-1000 bar), is summarised in Appendix A.

Much of the MRL work has been carried out in deep ocean waters, at salinities *ca* 35 ppt [1,2].

From Chen and Millero's equation of state, the specific volumes, thermal expansibilities and isothermal compressibilities of seawater at 35 ppt and at various temperatures and pressures have been calculated (Tables 3, 4), these values having a precision within $\pm 2 \times 10^{-8}$ m^3 kg^{-1} in V^T, $\pm 4 \times 10^{-6}$ degree^{-1} in α^P and $\pm 0.10 \times 10^{-8}$ kPa^{-1} in β^P and agreeing within these limits with those values obtained experimentally.

As mentioned above, the density of seawater, specific volume and the density factor, $\sigma(S,T,P)$, are complementary (eqns.1, 12, 13). Using the data from Table 3, one can calculate $\sigma(35,T,P)$ and compare the values so obtained with those at atmospheric pressure for $\sigma_T(S,T)$, using eqn.6 or hydrological tables [10,11]. This comparison has been carried out for certain selected values at 35 ppt salinity (Table 5), under conditions similar to those experienced in the field (for example, Station H, in Ref.2). The results indicate that the density of seawater in situ is greater than that at atmospheric pressure and that the effect of pressure (depth) on density is considerably greater than that of temperature.

At the working level, accurate calculations can be carried out (Appendix A) but often simplified equations may suffice for particular needs.

From a comparison of results calculated for $\sigma(S,T,P)$ over the temperature range 0-25°C and range of depths 0-4000 m (0-40 MPa, 0-400 bar) in seawater [25], salinity 35 ppt, one obtains

$$\frac{\Delta\sigma}{\Delta P}\ (35,T,P) \ \simeq \ 4.56 \times 10^{-4} - 1.67 \times 10^{-6}T \quad (kPa)^{-1} \tag{17}$$

and

$$\frac{\Delta\sigma}{\Delta T}\ (35,T,P) \ \simeq \ -0.190 - 1.67 \times 10^{-6}P \quad (degree)^{-1} \tag{18}$$

where T is the temperature in degrees (C) and P is the pressure in kPa.

Eqn.17 is very similar to that proposed by Defant, eqn.14, while eqn.18 is a more generalised form of eqn.8. However, there is a difference between the temperature coefficients defined by eqn.8 and eqn.18. Eqn.18 is intended to account for small changes in σ_T or, more correctly $\sigma(S = 35,T,P = 100$ kPa), over a range of $\pm$ 1°C, quite accurately, whereas eqn.18 gives a reasonable approximation ($\pm$ 0.05) to changes in $\sigma(S = 35,T,P)$ over a large range of both temperatures (0-25°C) and pressures (0-40 MPa, 0-400 bar).

4. AN APPLICATION OF THESE RESULTS

The author's attention to the problem of the effect of pressure on the density of seawater arose out of discussions on the significance of the results of the MRL Indian Ocean programme [2] in relation to the vertical stratification and the circulation and mixing of water masses at various stations.

At certain stations, it appeared as if there were strata in the ocean where more dense layers of water were residing over less dense layers of water, these layers being identified on the basis of Sigma-T values calculated from salinity and temperature data alone [11]. It was only after a depth correction, or more correctly, a pressure correction, calculated from Chen and Millero's equation of state (Appendix A), that these apparent anomalies were rectified. It is hoped to cover this in more detail in a future report.

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THE RELATION BETWEEN SIGMA-T, TEMPERATURE AND SALINITY IN NATURAL
SEAWATER, FOLLOWING COX, McCARTNEY AND CULKIN (1970)

$$\sigma_T(T,S) = \sum_i \sum_j a_{ij} T^i S^j \qquad 0 \leqslant i, j \leqslant 3$$

$$= a_{0\,0} + a_{1\,0} T + a_{0\,1} S + a_{2\,0} T^2$$

$$+ a_{1\,1} ST + a_{0\,2} S^2 + a_{3\,0} T^3 + a_{2\,1} T^2 S$$

$$+ a_{1\,2} TS^2 + a_{0\,3} S^3$$

The polynomial coefficients $a_{i,j}$ apply :

i	j	a_{ij}
0	0	$8.00969062 \times 10^{-2}$
	1	$7.97018644 \times 10^{-1}$
	2	$1.31710842 \times 10^{-4}$
	3	$-6.11831499 \times 10^{-8}$
1	0	$5.88194023 \times 10^{-2}$
	1	$-3.25310441 \times 10^{-3}$
	2	$2.87971530 \times 10^{-6}$
2	0	$-8.11465413 \times 10^{-3}$
	1	$3.98187483 \times 10^{-5}$
3	0	$4.76600414 \times 10^{-5}$

The formula was derived from seawater samples with $25 \geqslant T \geqslant 0°C$, $41 \geqslant S \geqslant 9$
ppt, (Ref. 11).

THE VARIATION OF SIGMA-T FOR NATURAL SEAWATERS WITH CHANGES
IN TEMPERATURE AND SALINITY

	σ_T	σ_T	σ_T	σ_T
	(25°C, 35 ppt)	(26°C, 35 ppt)	(25°C, 36 ppt)	(26°C, 36 ppt)
Eqn. 7	23.38_3	23.07_1	24.13_5	23.82_1
Eqn. 6	23.37	23.07	24.13	23.82
Ref. 10	23.37	23.07	24.13	23.83

	σ_T	$-$	σ_T
	(25°C, 35 ppt)		(26°C, 35 ppt)
Eqn. 8		0.30	
Eqn. 6		0.30	
Ref. 10		0.30	

	σ_T	$-$	σ_T
	(25°C, 35 ppt)		(25°C, 36 ppt)
Eqn. 9		-0.75	
Eqn. 6		-0.76	
Ref. 10		-0.76	

T A B L E   3

THE SPECIFIC VOLUMES AND DENSITIES OF SEAWATER AT 35 ppt SALINITY
AND VARIOUS TEMPERATURES AND PRESSURES, FOLLOWING
CHEN AND MILLERO (REF.14)

$$10^3 V \quad (m^3 \ kg^{-1})$$

P (kPa)	Temperature (C)					
	0	5	10	15	20	25
0	0.97266	0.97307	0.97375	0.97469	0.97583	0.97719
10000	0.96823	0.96875	0.96953	0.97053	0.97173	0.97313
20000	0.96393	0.96456	0.96542	0.96649	0.96775	0.96918
30000	0.95975	0.96049	0.96144	0.96257	0.96388	0.96534
40000	0.95570	0.95654	0.95756	0.95876	0.96010	0.96161

$$10^{-3} \rho \quad (kg \ m^{-3})$$

P (kPa)	Temperature (C)					
	0	5	10	15	20	25
0	1.0281	1.0276	1.0269	1.0260	1.0248	1.0233
10000	1.0328	1.0323	1.0314	1.0304	1.0291	1.0276
20000	1.0374	1.0367	1.0358	1.0347	1.0333	1.0318
30000	1.0419	1.0411	1.0401	1.0389	1.0375	1.0359
40000	1.0464	1.0454	1.0443	1.0430	1.0416	1.0399

T A B L E   4

THE THERMAL EXPANSIBILITIES AND ISOTHERMAL COMPRESSIBILITIES OF SEAWATER AT 35 ppt AND VARIOUS TEMPERATURE AND PRESSURES, FOLLOWING CHEN AND MILLERO (REF.14)

$$10^6 \alpha^P \quad (\text{degree, } °C)^{-1}$$

P (kPa)	Temperature (°C)					
	0	5	10	15	20	25
0	51.74	113.5	166.8	214.2	257.2	297.0
10000	79.29	135.7	184.7	228.5	268.5	305.6
20000	105.3	156.7	201.7	242.2	278.3	314.1
30000	129.7	176.6	217.9	255.2	289.7	322.2
40000	152.8	195.4	233.1	265.6	299.6	330.0

$$10^8 \beta^P \quad (\text{kPa})^{-1}$$

P (kPa)	Temperature (°C)					
	0	5	10	15	20	25
0	46.3	45.1	44.1	43.2	42.6	42.1
10000	45.1	43.9	43.0	42.2	41.6	41.3
20000	43.9	42.8	41.9	41.2	40.6	40.2
30000	42.8	41.7	40.9	40.2	39.6	39.2
40000	41.7	40.7	39.9	39.2	38.7	38.3

T A B L E 5

COMPARISON OF SIGMA (S,T,P) AND SIGMA (S,T) AT 35 ppt SALINITY, AFTER
CHEN AND MILLERO (REF. 14)

Temp (C)	Pressure (kPa)	Specific Volume $10^3 v^P(35,T,p)$ $(m^3 \ kg^{-1})$	Density $10^{-3}\rho(35,T,p)$ $(kg \ m^{-3})$	$\sigma(35,T,P)$ (eqn. 12)	$\sigma(35,T)$ Ref.10	$\sigma(35,T)$ Ref.14
25	0	0.977189	1.02334	23.34	23.38	23.34
15	2000	0.973855	1.02685	26.85	25.97	26.00
10	4000	0.972063	1.02874	28.74	26.96	26.97
5	10000	0.969750	1.03226	32.26	27.67	27.69
3	20000	0.964305	1.03702	37.02	27.85	27.92
2	30000	0.960048	1.04161	41.61	27.94	27.99
0	0	0.972664	1.02810	28.10	28.10	28.13
25	0	0.977189	1.02334	23.34	23.38	23.34
0	40000	0.955707	1.04634	46.34	28.10	28.13
25	40000	0.961610	1.03992	39.92	23.38	23.34

APPENDIX A

CHEN AND MILLERO EQUATION OF STATE OF SEAWATER (1978)

(a) Density of Pure Water, ρ_w^o, at Atmospheric Pressure, (100 kPa, 1 bar)

$$\rho_w^o = 999.8395 + 6.7914 \times 10^{-2}\ T$$
$$-9.0894 \times 10^{-3}\ T^2 + 1.0171 \times 10^{-4}\ T^3$$
$$-1.2846 \times 10^{-6}\ T^4 + 1.1592 \times 10^{-8}\ T^5$$
$$-5.0125 \times 10^{-11}\ T^6$$

where T is the temperature (°C) and the density is in kg m^{-3}.

(b) Density of Seawater, ρ_{sw}^o, at Atmospheric Pressure, (100 kPa, 1 bar)

$$\rho_{sw}^o = \rho_w^o + LS + MS^{3/2} + NS^2$$

where S is the salinity, ppt,

$$L = 8.25917 \times 10^{-1} - 4.4490 \times 10^{-3}\ T$$
$$+ 1.0485 \times 10^{-4}\ T^2 - 1.2580 \times 10^{-6}\ T^3$$
$$+ 3.315 \times 10^{-9}\ T^4$$

$$M = -6.33761 \times 10^{-3} + 2.8441 \times 10^{-4}\ T$$
$$-1.6871 \times 10^{-5}\ T^2 + 2.83258 \times 10^{-7}\ T^3$$

and

$$N = 5.4705 \times 10^{-4} - 1.97975 \times 10^{-5}\ T$$
$$+ 1.6641 \times 10^{-6}\ T^2 - 3.1203 \times 10^{-8}\ T^3$$

(c) Specific Volume of Seawater, V^o, at 1 atm.

$$V^o = 1/\rho_{sw}^o$$

(d) Second degree Secant Bulk Modulus, K

$$K = \frac{P\ V^o}{V^o - V^P} \qquad \text{(by definition)}$$

where P is the pressure,   and V^P is the specific volume of seawater at this pressure.

Assume

$$K = K^o + AP + BP^2$$

where K^o is the secant bulk modulus of seawater at zero pressure, the arbitrarily defined reference, and K^o, A and B are salinity and temperature dependent variables.

$$K^o = K_w^o + a(T)\ S + b(T)\ S^{3/2} \qquad \text{(kPa)}$$

$$A = A_w^o + c(T)\ S + d(T)\ S^{3/2}$$

$$B = B_w^o + e(T)\ S \qquad \text{(kPa)}^{-1}$$

where

K_w^o, A_w^o and B_w^o are the coefficients relating to pure water and the functions $a(T),\ldots\ldots,e(T)$ are the temperature-dependent variables relating salinity to K, A and B.

$$K_w^o = 1.965217 \times 10^6 + 1.48183 \times 10^4\ T$$
$$-2.29995 \times 10^2\ T^2 + 1.2810\ T^3$$
$$-4.91564 \times 10^{-3}\ T^4 + 1.03553 \times 10^{-5}\ T^5$$

$$A_w^o = 3.26138 + 5.223 \times 10^{-4}\ T + 1.324 \times 10^{-4}\ T^2$$
$$-7.655 \times 10^{-7}\ T^3 + 8.584 \times 10^{-10}\ T^4$$

$$B_w^o = 7.2061 \times 10^{-7} - 5.8948 \times 10^{-8}\ T$$
$$+ 8.699 \times 10^{-10}\ T^2 - 1.010 \times 10^{-11}\ T^3$$
$$+ 4.322 \times 10^{-14}\ T^4.$$

$$a(T) = 5375.1 - 46.07\ T - 0.703\ T^2$$
$$-5.107 \times 10^{-3}\ T^3$$

$$b(T) = 23.22 - 0.4838\ T$$

$$c(T) = 4.692 \times 10^{-3} - 8.387 \times 10^{-5}\ T$$
$$+ 4.68 \times 10^{-7}\ T^2$$

$$d(T) = -1.332 \times 10^{-4}$$

$$e(T) = -1.412 \times 10^{-8} + 9.006 \times 10^{-10}\ T$$
$$-1.551 \times 10^{-11}\ T^2$$

(e) <u>Thermal Expansibility</u>

$$\alpha^P = (1/V^P)\ (\partial V/\partial T)$$

(f) <u>Thermal Compressibility</u>

$$\beta^P = (-\ 1/V^P)\ (\partial V/\partial P)$$

Simple computer programs can easily be written on the basis of these equations, where one calculates K. One can then evaluate V^P and $\rho(S,T,P)$.

APPENDIX B

UNITS OF DENSITY AND PRESSURE

Throughout this paper, SI units have been used. Even though the use of cgs units still persists throughout the oceanographic literature, the use of SI units has been recommended for almost a decade (25) and, in this paper, the author bows to the march of progress.

The SI unit of pressure is the pascal, Pa. The practical unit of pressure used previously was the atmosphere, the pressure exerted per square centimetre by a column of mercury 760 mm high at a temperature of 0°C where the acceleration of gravity is 980.665 cm s^{-2}.

The following conversions apply :

density	1 g cm^{-3}	=	1×10^3 kg m^{-3}
pressure	1 atm	=	1.0133×10^5 Pa
	1 bar	=	1.00×10^5 Pa
		=	100 kPa
	1 dyne cm^{-2}	=	1.00×10^{-1} Pa where
	1 Pa	=	1 N m^{-2}

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